

# SCIENCE FOR GLASS PRODUCTION

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## FILM FORMATION IN THE $\text{Bi}_2\text{O}_3 - \text{TiO}_2 - \text{Fe}_2\text{O}_3$ TERNARY SYSTEM

A. B. Atkarskaya<sup>1</sup> and V. I. Kiyan<sup>1</sup>Translated from *Steklo i Keramika*, No. 12, pp. 5 – 8, December, 1999.

The processes of film formation in a ternary system are studied, beginning with the preparation of the working solution and up to coat firing. It is demonstrated that the properties and quality of a coating are determined at the stage of preparing a film-forming solution and depend on the size and shape of the sol particles, the film porosity, and the diffusion process at the glass-film interface.

The availability and inexpensiveness of sol-gel technology make it very expedient for modification of glass surfaces with the aim of imparting new non-traditional properties to ordinary sheet glass.

Processes occurring in film production are complicated: the technology includes elements of chemistry, physical chemistry, the physics of liquid and solid bodies, and the technology of nonmetallic materials, in particular, glass and ceramics. At the same time, knowledge of these processes makes it possible to control them and, consequently, obtain modified articles with preset properties.

The purpose of the present paper is to study film formation in the  $\text{Bi}_2\text{O}_3 - \text{TiO}_2 - \text{Fe}_2\text{O}_3$  ternary system, starting with the preparation of initial solutions and ending with coating firing.

The initial materials for film-forming solutions (FFS) were the chemicals listed in Table 1.

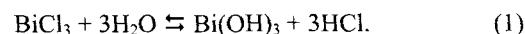
It was found experimentally that the optimum weight content of a multicomponent FFS for the deposition conditions accepted in the research is 5%, i.e., the total content of all film-forming oxides should be 5%. Therefore, all initial one-component solutions also contained 5% oxides.

A specific feature of sol-gel technology is the use of volatile low-boiling liquids as solvents. We selected ethanol since it equally well dissolves all initial components, is readily available, and is relatively non-toxic.

Hydrochloric acid is needed to develop the optimum acidity in the FFS and regulate the stability level of sol-gel systems.

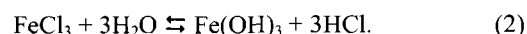
A sample of bismuth oxide was dissolved in hydrochloric acid and diluted with ethanol to the working concentration level. If symptoms of  $\text{BiCl}_3$  hydrolysis manifested in the

turbidity of the solution were observed, 1 – 2 drops of HCl was added and the following equilibrium was shifted to the left:



Note that precipitation of bismuth hydroxide proceeds in a weakly acid or neutral medium at  $\text{pH} \leq 7$  [1].

Ferric oxide was dissolved in ethanol. The solution is capable of preserving its clarity for one or more months, depending on the moisture of ferric oxide crystal hydrate and the amount of water in ethanol, after which a sediment is formed:



To prevent sedimentation, an excess of hydrochloric acid is needed, which shifts equilibrium (2) to the left. Sedimentation of  $\text{Fe}(\text{OH})_3$  starts at  $\text{pH} = 2.2$  [1].

Titanium alkoxide solution in absolute alcohol retains its clarity for an indefinitely long period, and when diluted by 96% ethanol is instantly hydrolyzed with water impurity according to the reaction



TABLE 1

Initial material	Weight content of main substance, %	Introduced oxide
Bismuth oxide, "chemically pure"	99.5	$\text{Bi}_2\text{O}_3$
Ferrous chloride hexahydrate, "analytical grade"	98.0	$\text{Fe}_2\text{O}_3$
Titanium tetraethoxide, "pure"	98.0	$\text{TiO}_2$
Titanium tetrabutoxide, "pure"	97.0	$\text{TiO}_2$

<sup>1</sup> Avtosteklo Production Company.

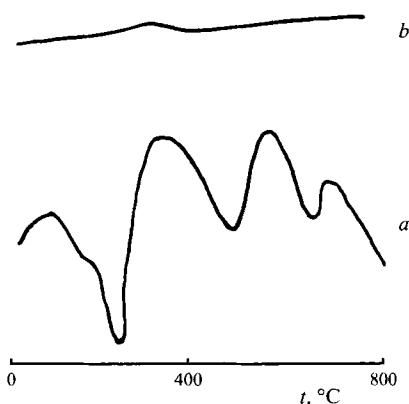
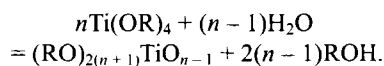


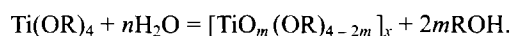
Fig. 1. DTA curves of powders with identical compositions obtained by sol-gel technology (a) and by the classical method (b).

To prevent this, dissolution is performed in a hydrochloric-acid-alcohol mixture with  $\text{pH} < 2$  ( $\text{pH}$  of  $\text{Ti}(\text{OH})_4$  sedimentation is equal to 2 [1]).

The detailed mechanism of hydrolysis of titanium esters is thus far not perfectly clear [2]. The essential factor is the fact that the hydrolysis process is accelerated with rising temperature and increasing amount of water. If the amount of water is insufficient for complete hydrolysis, intermolecular condensation takes place, accompanied by the formation of polymeric compounds. If the  $\text{H}_2\text{O} : \text{Ti}(\text{OR})_4$  ratio is below 1, linear polymers in hydrolysis are formed according to the reaction [2]

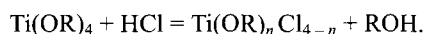


With a water consumption above 1 but below 1.5 mole per mole of ester, polymers with cross-lateral bonds should be formed [2]:



Calculations show that the ratio  $\text{H}_2\text{O} : \text{Ti}(\text{OR})_4$  in the studied FFS increases with increasing  $\text{Bi}_2\text{O}_3$  content; therefore hydrolysis of titanium esters in this system can end either in the formation of polymers or the formation of  $\text{Ti}(\text{OH})_4$  sediment as a result of complete hydrolysis of alkoxide. Hence, it can be expected that the shape of the sol particles in FFS of different compositions will be modified from chains of different lengths to spheroid particles.

At the same time, the formation of halogen esters in titanium-bearing solutions under the effect of hydrochloric acid is possible according to the reaction [2]



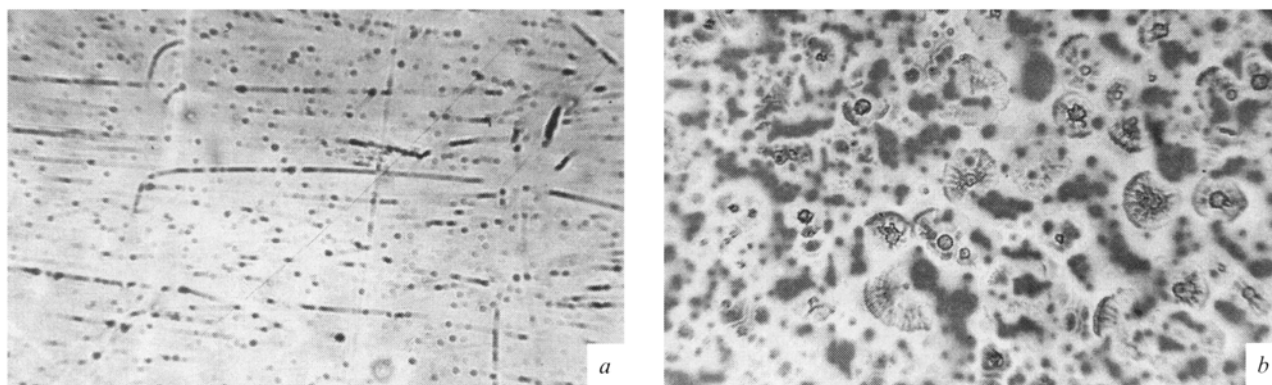
For instance, butoxytrichlorotitanium  $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$  with a boiling point of  $65 - 80^\circ\text{C}$  [2] was identified by us in ethyl distillate obtained from used FFS.

A complex FFS is produced by mixing initial solutions in the required proportions with subsequent holding for 1–2 days for the purpose of creating a sol with the optimum properties. In this case, the quantities of acid and water introduced with one-component solutions are “averaged.” The FFS acquires averaged  $\text{pH}$ , which stimulates hydrolysis or dissolution of components according to reactions (1)–(3) and gives rise to the seeds of a disperse phase, whose size and quantity are closely related to the composition and  $\text{pH}$  of the solution.

The shape of the sol particles presumably to a large extent depends on the ratio  $\text{H}_2\text{O} : \text{Ti}(\text{OR})_4$  in the complex solution. With increasing content of  $\text{Bi}_2\text{O}_3$  introduced instead of  $\text{TiO}_2$ , disperse particles should transform from chain-shaped to spheroid particles of various lengths and diameters. This will be facilitated by the decreased content of polymer-forming, titanium-containing component in the solution and (or) increased amount of water introduced into the system with alcohol, hydrochloric acid, and ferric chloride crystal hydrate, i.e., the higher the content of  $\text{Bi}_2\text{O}_3$  in the solution, the less stable the solution. Indeed, whereas the solution used to produce a film with  $\text{Bi}_2\text{O}_3$  molar content equal to 10% is optically transparent for 1.5–2 months or more, the FFS corresponding to the film with 70%  $\text{Bi}_2\text{O}_3$  becomes turbid on the 5–7th day. Moreover, with aging of the solution and intensification of the hydrolysis processes in it, the particles apparently modify their shape from chain-like to spheroid. Such phenomena are actually observed in the system studied.

Since the particle size of the FFS sol disperse phase is very small [3], the solid component of the solution has a well-developed surface and, accordingly, high surface energy. This facilitates the reactions between the components, decomposition of hydrolysis products, etc. They all proceed at a lower temperature than in the classical technology. For instance, traces of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ , i.e., products of the decomposition of iron and titanium hydroxides, as well as traces of pseudobrookite  $\text{Fe}_2\text{TiO}_5$ , were identified in the powder produced from an FFS in the way described in [4] and dried at  $80^\circ\text{C}$ . Iron hydroxide in a classical variant decomposes at a temperature of  $150 - 200^\circ\text{C}$  [5], titanium hydroxide decomposes at  $500^\circ\text{C}$  [2], and  $\text{Fe}_2\text{TiO}_5$  is produced at  $1200^\circ\text{C}$  [2].

Figure 1 shows thermograms of ternary powders with identical compositions produced by the sol-gel technology and the traditional method of mixing initial materials. The first thermogram is characterized by strong exothermic and endothermic effects, which points to decomposition and other reactions between the components. The second curve does not exhibit noticeable traces of chemical reactions. This confirms the assumption of high chemical activity of sol-gel products. Note that the size of the particles in the FFS should be significantly smaller than in the powder, due to the specifics of powder production. Therefore, it can be assumed that reactions in solution and in film will proceed at even lower temperatures than in sol-gel powders.



**Fig. 2.** Microphotos of films with molar composition 20%  $\text{Bi}_2\text{O}_3$ , 25%  $\text{Fe}_2\text{O}_3$ , and 55%  $\text{TiO}_2$  produced by applying 2-day (a) and 16-day (b) solutions and dried at room temperature for 24 h ( $\times 100$ ).

In the beginning, when a solution is deposited on a glass surface, the layer is firmly fixed due to the wettability and the presence of adhesive forces, which are probably accompanied by primary diffusion phenomena at the interphase boundary: the film and glass components mutually penetrate into each other and form the adhesive transitional layer. It has been noted that the higher the bismuth oxide content in the FFS, the worse the glass substrate wettability. This is possibly due to the high surface tension of such solutions.

As the film dries in air, the solvent (alcohol, excessive hydrochloric acid) evaporates, which is inevitable in preparing a complex FFS, due to the "averaging" of three solutions and possible release of hydrochloric acid as a consequence of component interaction. Under the effect of air moisture, reactions of hydrolysis and polycondensation end and result in the formation of titanium-organic polymers with both longitudinal and lateral bonds [2].

Simultaneously with evaporation, i.e., a decrease in the solvent concentration, the film components are partly crystallized, including the initial products not participating in reactions, the hydrolysis products, and the reaction products. The film not subjected to heat treatment retains a sufficient amount of moisture preserved in gel created by the FFS layers stuck to the glass. In other words, a moist coating is an amorphous body, in which the crystallization products are uniformly distributed (Fig. 2a). Wet film visually is uniform and transparent. However, the refraction index and the mirror reflection coefficient are 10–20% lower than in fired films. This is related to the presence of a significant quantity of water in the coating, which decreases the refractive index of a solid body according to the equation [6]

$$n_{\text{ef}} = n_1 - \Pi(n_1 - n_3) - (n_2 - n_3)f(P/P_0),$$

where  $\Pi$  is porosity,  $n_1$  is the refractive index of the skeleton material of the solid body,  $n_2$  and  $n_3$  are the refractive indices of water (1.33) and air (1.00), respectively, and  $f(P/P_0)$  is the equation of absorption isotherm in the general form.

The strength parameters of a dry coating not subjected to heat treatment are worse than those of a fired coating. The fired coating Vickers microhardness is 15–25% higher.

Diffusion processes continue in a drying film: the boundary layer becomes 5–10% thicker, and the concentration of sodium, calcium, and silicon migrating from a glass substrate to the coating increases.

After drying in air at room temperature, the glass with film coating is fired at a temperature of 550°C. As is shown by experience, a glass sheet above that temperature is perceptibly deformed. Reactions of dehydration, crystallization, decomposition, melting, and interaction take part in the coating layer, which is supported by the data in Fig. 1. All processes proceed at a lower temperature than in the traditional mixture of raw materials, due to high dispersion and high chemical activity of the sol-gel products. Vitrification in them also proceeds at a low temperature. The evidence of this is the visual control of two powders after differential thermal analysis, i.e., heated to 800°C. The traditional powder is a compact cake, whereas the sol-gel product is a vitrified material with 70–80% vitreous phase. The x-ray phase analysis data for these powders are presented below.

Classical Powder	Sol-Gel Product
$\text{Fe}_2\text{TiO}_5$ — 126 . . . . .	$\text{Fe}_2\text{TiO}_5$ — 89
$\text{TiO}_2$ — 107 . . . . .	$\text{TiO}_2$ — 49
$\text{Fe}_2\text{O}_3$ — traces . . . . .	$\text{Fe}_2\text{O}_3$ — 48

These data indicate that the sol-gel products are less crystallized and substantiate the visual inspection results.

Assuming that the particle size and FFS in film is smaller, it can be suggested that vitrification in coatings proceeds at an even lower temperature than in the sol-gel powders. Indeed, the x-ray phase analysis data for thin films of the compositions considered indicate their high degree of amorphousness: only slight traces of  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$  are present in some of them. In order to obtain a film of thickness sufficient for x-ray phase analysis, they were multiply deposited on a glass substrate.

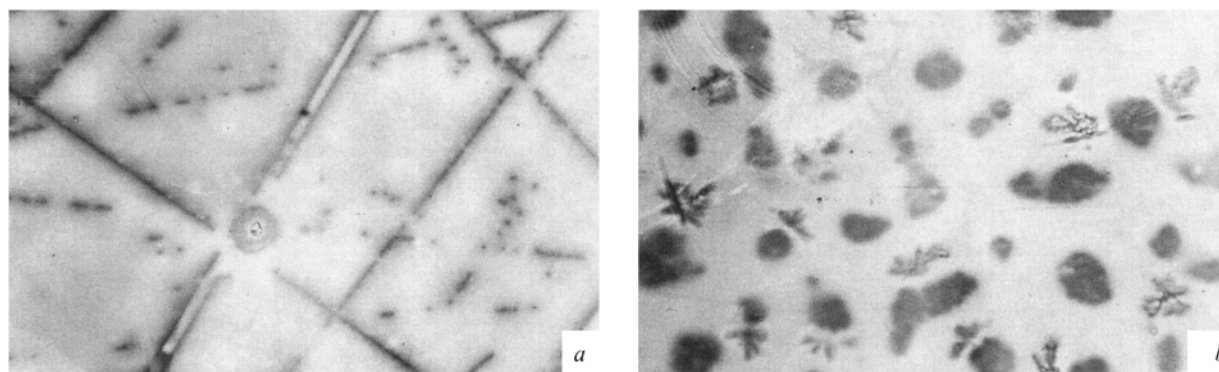


Fig. 3. Microphotos of heat-treated films with molar composition 20%  $\text{Bi}_2\text{O}_3$ , 25%  $\text{Fe}_2\text{O}_3$ , and 55%  $\text{TiO}_2$  produced by applying 2-day (a) and 16-day (b) solutions ( $\times 100$ ).

Some authors suggest that inhomogeneities in sol-gel products are determined at the solution preparation stage [7]. This is substantiated by the results of the present study. Figure 2a and b shows the microphotos of films with an identical molar composition produced from FFS of different ages. The shape and the number of inclusions in the coatings differ significantly. The dried film made from the 2-day solution exhibits chain-shaped inclusions. As an FFS ages, hydrolysis processes evolve in and are intensified due to the penetration of air moisture into the multiply used solution. This contributes to a modification of the physical parameters of the FFS: the kinematic viscosity of the 2-day solution is  $2.576 \text{ cm}^2/\text{sec}$ , and that of the 16-day solution is  $2.230 \text{ cm}^2/\text{sec}$ . According to the basic concepts of colloid chemistry [3], this suggests either a modification of the particle shape or an increased content of the dispersed phase. The first possibility is more probable in our case, since the two-dimensional polymers are formed in titanium-bearing solutions with a limited

amount of water. An increase in the water content deepens the extent of hydrolysis and disturbs the conditions of the formation of chain structures (Fig. 2b). The dried film produced by application of the 16-day solution exhibits spheroid inclusions.

The following structural modifications are observed in coatings after heat treatment: chain particles (Fig. 2a) evolve and form a continuous branched lattice (Fig. 3a). Such a structure has a strengthening effect; therefore, the Vickers microhardness is rather high: 7116 – 6766 MPa.

The spheroid particles (Fig. 2b) in firing are enlarged, and their number decreases (Fig. 3b). The microhardness decreases to 6720 – 6506 MPa.

In heating dried films, gel is dehydrated, chlorides decompose, and alkoxy groups are removed. All this contributes to the formation of a porous body. The higher the firing temperature, the higher the probability of pore sealing and the lower the coating porosity. Evidence of this is the variation in the refractive index (Table 2), which is indirectly a function of the solid-body porosity [6]. The higher the porosity, the lower the refractive index.

As can be seen, with increasing temperature the refractive index of the coating increases. It should be noted that such regularity is not always observed. The deviations, as a rule, are related to crystallization processes evolving in the films of certain compositions.

An increase in the firing temperature intensifies the migration of components from glass to film and vice versa. However, a decrease in porosity delays this process (Table 3). In fact, with increasing temperature, the total content of migrating ions decreases.

Thus, the stability of film-forming solutions in the  $\text{Bi}_2\text{O} - \text{TiO}_2 - \text{Fe}_2\text{O}_3$  system is proportionally related to the quantity of  $\text{Bi}_2\text{O}_3$  in them. The high degree of dispersion of the FFS solid phase and film particles facilitates the chemical reactions and vitrification processes at decreased temperatures. This ensures high chemical activity of the initial sol-gel products. The structure of sol-gel films is determined at the FFS preparation stage and is extremely sensitive to its

TABLE 2

Molar content of $\text{Bi}_2\text{O}_3$ in film, %	Refractive index of films fired for 30 min at a temperature of	
	350°C	450°C
10	2.115	2.193
30	2.144	2.160
60	2.042	2.076

TABLE 3

Firing temperature, °C	Molar content of migrating oxides, %			Transitional-layer size, Å, for elements		
	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{SiO}_2$	Na	Ca	Si
350	24.7	3.4	4.3	6960	7060	7000
450	18.1	4.4	0.0	6520	6420	6560

age. An increase in the temperature of film firing results in the formation of a solid body with a certain degree of porosity, which affects the film properties and the diffusion processes at the glass-film interface.

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